

## ELECTRICAL CONDUCTIVITY AND DIELECTRIC RELAXATION OF LITHIUM ALUMINO BORATE GLASSES

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### ABSTRACT

Ion conducting glasses  $30\text{ Li}_2\text{O}:(70-\text{X})\text{ B}_2\text{O}_3:\text{X Al}_2\text{O}_3$  have been prepared over wide range composition ( $\text{X} = 0, 5, 10, 15$  and  $20$  mole %). The mixed former effect on lithium ion transport due to addition of  $\text{Al}_2\text{O}_3$  in series of Lithium borate glasses have been investigated. The electrical conductivity and dielectric relaxation of these glasses was analyzed using Aligent LCR analyzer in frequency range (1Hz – 1MHz) at different temperature (323k – 623k). The decrease in conductivity with the addition of  $\text{Al}_2\text{O}_3$  attributed to structural modification and formation of B – O – Al Linkage resulting in reduces migration of  $\text{Li}^+$  ions along these bonds. The dielectric constants and modulus formalism is used to described the dielectric relaxation.

**KEYWORDS:** Electrical Conductivity, Dielectric Constants, Relaxation Frequency, Mixed Former Effect

### INTRODUCTION

The ionic conductivity of glasses has been widely investigated [1, 2] and special attention has been devoted to lithium conductor glasses due to their applicability as solid electrolytes in lithium cells [3]. The electrical conductivity of ionic glasses may be increased by dissolving halides or other salts in the glass structure [4, 5] by mixing a second glass former in an originally binary glass constituted by glass former and glass modifier. In fact, the non-additive increase in electrical conductivity, observed when a second former is added to binary glass, is known as mixed former effect [1]. The most classical and remarkable examples of the mixed former effect was found at the borophosphate system [6] in which the conductivity of the most conductive ternary composition are two order of magnitude higher than that of binary glasses. In this system, the binary composition Lithium borate and Lithium Phosphate, present very similar electrical conductivities values. The mixed former effect has also been found in other glass system such as silver boro Phosphate [7], Lithium borophosphate [5], Lithium silicatelurate [8] and Lithium selenoborate [9]. However, if both binary glasses at the given system present very different electrical conductivities, a monotonic change (when the first former substituted by second one) of electrical conductivity with no maximum, may not be considered a mixed former effect.

Among Lithium base glass electrolyte, Lithium borophosphate glass have been studied extensively in the Literature [10-12] because of their tweeting structural and physical property changes upon network modifications. These system contain two former (B to P) in the glass network responsible for an enhancement in the ionic conductivity. The increase in conductivity is due to replacement of one former (P) by other one (B) and formation of various borate and phosphate structural unit in the glass network, if the total ion concentration is kept constant.

In present work deals with electrical conductivity and relaxation frequency of glass in the Lithium aluminoborate system containing 30 mole percent of  $\text{Li}_2\text{O}$ .

## EXPERIMENTAL

Glasses of composition  $30\text{Li}_2\text{O} : (70-x)\text{B}_2\text{O}_3 : x\text{Al}_2\text{O}_3$  where ( $x = 0, 5, 10, 15$  and  $20$  mol %) were prepared by melt quenching method, using high purity AR grade chemicals (Merc Laboratory) Lithium Carbonate ( $\text{Li}_2\text{CO}_3$ ), Boric acid ( $\text{H}_3\text{BO}_3$ ) and aluminum oxide ( $\text{Al}_2\text{O}_3$ ). Mixture of these materials in appropriate proportion were taken in alumina crucible and melted at temperature range from  $900 - 1100^\circ\text{C}$  depending upon the composition. The homogeneous melts were quenched in aluminum mould. The glass samples were annealed below their glass transition temperature ( $T_g$ ). The glasses were checked by X-ray diffraction (XPER PRO Diffractometer). The XRD pattern did not show any sharp peaks. This confirms the amorphous nature of the glass. The glass transition temperature was measured using differential thermal analysis instrument (NEEZ SCH STA 449F1) with heating rate  $10^\circ\text{C}/\text{min}$ . To study the surface morphology, scanning electron microscope technique was used.

Electrical properties and dielectric properties measurement were carried out by Aligent LCR analyzer for frequency  $10\text{Hz} - 1\text{MHz}$  in the temperature range  $323\text{K} - 623\text{K}$ . The sample holder assembly made by Pushpa scientific (2 terminal capacitor confirmation and spring loaded silver electrode) was used for all measurement. The sample temperature was measured by Pt - Cr thermocouples positioned very close to the sample. The temperature was controlled by using temperature controller and temperature constancy of  $\pm 1\text{K}$  was achieved in the entire range. Annealed circular glass pieces coated with silver paint on both side and having thickness of above  $0.1\text{cm}$  and diameter  $1\text{cm}$  were used for measurement.

## ANALYSIS OF DATA

The capacitance ( $C_p$ ) and conductance ( $G$ ) of all samples were measured from LCR analyzer. The conductivity of each sample was calculated by using expression.

$$\sigma = G (d/A) \quad (1)$$

Where  $d$  and  $A$  are the thickness and surface area of silver electrode.

The real ( $\epsilon'$ ) and imaginary ( $\epsilon''$ ) parts of dielectric constant were calculated from the relation.

$$\epsilon^*(\omega) = \epsilon'(\omega) + i\epsilon''(\omega) \quad (2)$$

Where  $\epsilon_0$  is the permittivity of free space and its value is  $8.854 \times 10^{-14}\text{F/cm}$ .

The data were analyzed using electric modulus formalism. The real ( $M'$ ) and imaginary ( $M''$ ) of complex dielectric modulus were obtained from  $\epsilon'$  and  $\epsilon''$  values using relation.

$$M' = \frac{\epsilon'}{(\epsilon'^2 + \epsilon''^2)} \quad (3)$$

$$M'' = \frac{\epsilon''}{(\epsilon'^2 + \epsilon''^2)} \quad (4)$$

## RESULTS AND DISCUSSIONS

### Dc Conductivity

The code composition of investigated glasses, glass transition temperature, dc conductivity at temperature 323K, activation energy and power law exponent are listed in Table 1. Tg-DTA curve of L1BA and SEM of sample L2BA and XRD Pattern of L2BA glass sample are shown in figure 1, 2, & 3 respectively. The XRD pattern confirms amorphous nature of glass. To study the surface morphology, scanning electron microscope result are obtained and it is clearly visible from these scan that for prepared glasses appears a homogenous structure of glass flake suggesting highly amorphous phase.

The variations of conductivity are all glasses are shown in figure 4 in  $\log \sigma$  plot as function of inverse temperature. It indicates that dc conductivity of all composition obey Arrhenius equation  $\sigma = \sigma_0 \exp(-E_{dc}/kT)$ .  $E_{dc}$  is activation energy and  $\sigma_0$  is exponential factor.

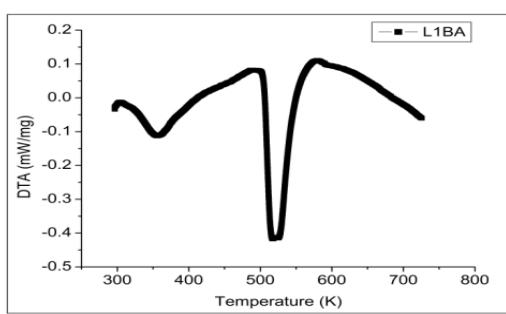


Figure 1: DTA Curve of L1BA

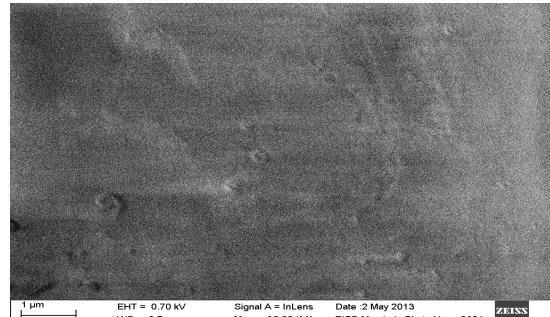


Figure 2: SEM Photograph of L2BA

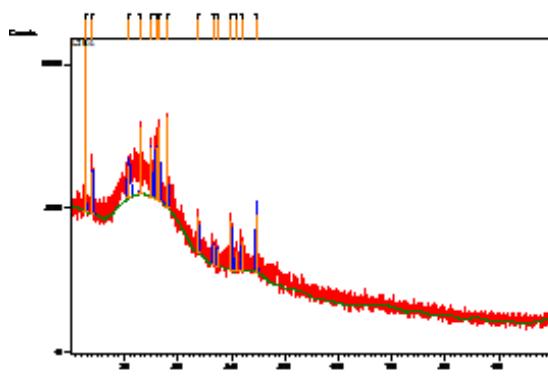


Figure 3: XRD of Sample L2BA

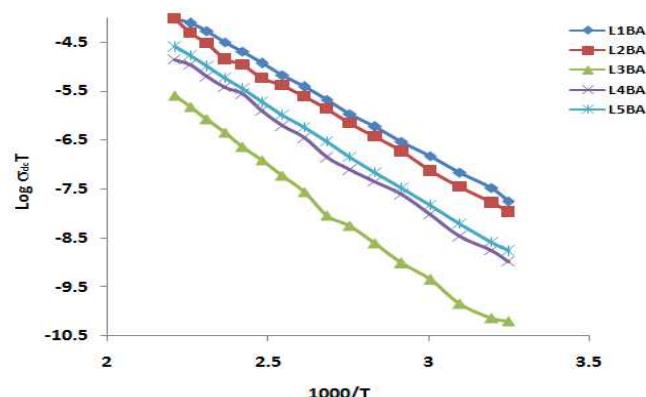


Figure 4: Log  $\sigma_{dc}T$  v/s  $1/T$

Table 1: Code, Composition, Tg, Activation Energy, Dc Conductivity and Power Exponent

Code	Mole % of $\text{Li}_2\text{O}$	Mole % of $\text{Al}_2\text{O}_3$	Mole % of $\text{B}_2\text{O}_3$	Tg(K)	$\sigma_{dc}$ S/cm	$E_{dc}$ (eV)	s
L1BA	30	0	70	500	6.44E-6	0.7214	0.819
L2BA	30	5	65	503	2.92E-7	0.9911	0.6161
L3BA	30	10	60	508	4.2E-7	0.8036	0.75
L4BA	30	15	55	512	4.2E-7	0.8036	0.625
L5BA	30	20	50	550	3.39E-6	0.7343	0.53

It is observed that glass sample L1BA exhibit high conductivity and low activation energy. The conductivity decreases with increase in mole percent of  $\text{Al}_2\text{O}_3$ . The decrease of conductivity is due to network regulation by formation B-O-Al and Al-O-Al bond and presence of large amount of  $\text{Al}_2\text{O}_3$  increases ionic character therefore it reduces Li ions mobility and brake conduction path [13]. Figure 5 shows variation of activation energy and DC conductivity with different composition of  $\text{Al}_2\text{O}_3$  which indicates mixed former effect does not exist in this composition.

### A. C. CONDUCTIVITY

The conductivity of samples with different frequency at temperature 623K is shown in figure 6. At low frequencies a random diffusion of ionic charge carrier via activated channels has been observed to result in frequency independent conductivity [13]. At high frequency conductivity exhibit dispersion increasing roughly in power law fashion. The ac conductivity of ionic conducting glasses over wide range of temperature and frequencies show region of power law behavior in the form [14-15].

$$\sigma(\omega) = \sigma_{dc} + A\omega^s$$

$A$  is the temperature dependant constant and  $s$  is the power exponent value obtained from 0 to 1 which represent degree of interaction between mobile ions with network for all investigated samples. For these samples,  $s$  component lying between 0.274-.819. The decreasing trends of  $s$  with temperature has been observed. The variation of  $s$  with temperature may be due to contributions from conducting and dielectric losses at different temperature [16-17]. The highest conductivity is observed for the L1BA sample,  $3.44 \times 10^{-7} \text{ S/cm}$  at temperature 323K and  $6.53 \times 10^{-6} \text{ S/cm}$  at temperature 623K for the frequency 1KHz. The values of  $s$  factor changes with composition which is reflected in the variation of  $T_g$  [18-19].

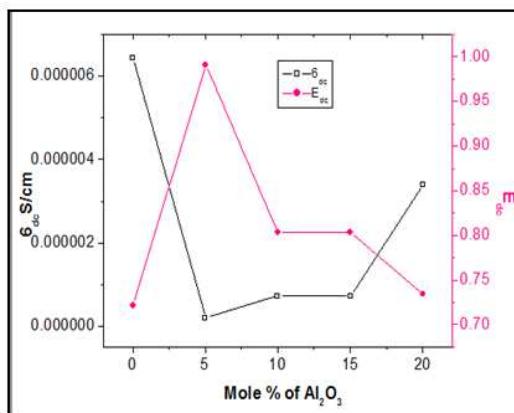


Figure 5: Variation of  $6_{dc}$  and  $E_{dc}$  with Content of  $\text{Al}_2\text{O}_3$

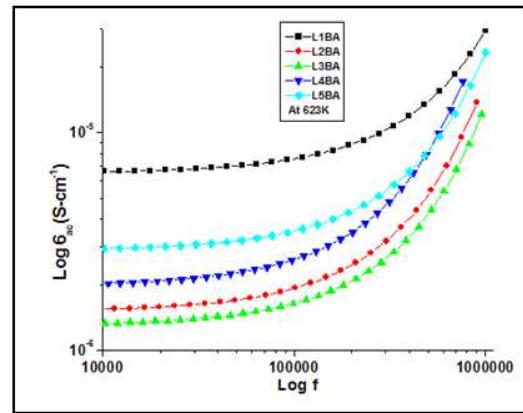


Figure 6: Logs  $\sigma_{ac}$  v/s Log f

### Dielectric Properties and Relaxation

The dielectric response of investigated samples has been explained by measuring both real and imaginary part of dielectric constant. The real part of dielectric content ( $\epsilon'$ ) represents the polarizability of the material where imaginary dielectric constant ( $\epsilon''$ ) represent the energy loss due to polarization and conduction. The dielectric materials have four distinguishable viz electronic, atomic, orientation and space charge polarization

The variation of dielectric constant ( $\epsilon'$ ) with frequency of L1BA glass sample at different temperature is shown in figure 7. At all temperature under investigation, dielectric constant ( $\epsilon'$ ) decreases with increase in frequency. The decrease

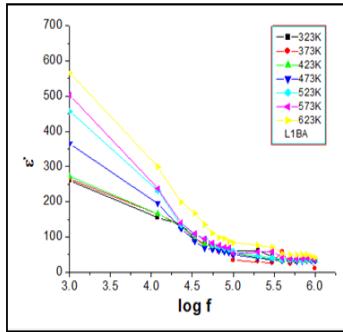
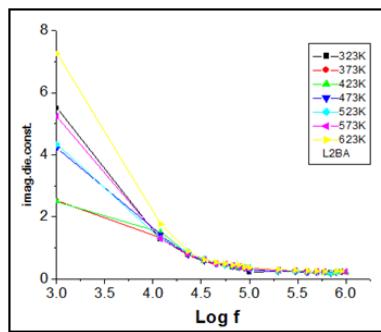
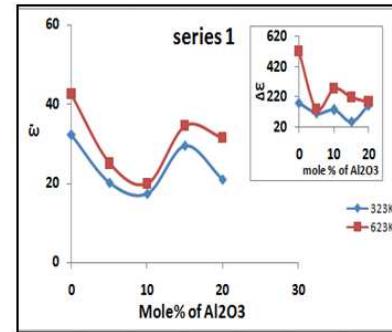
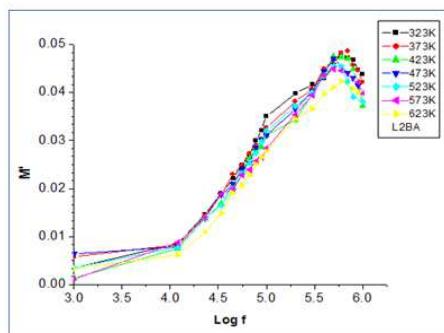
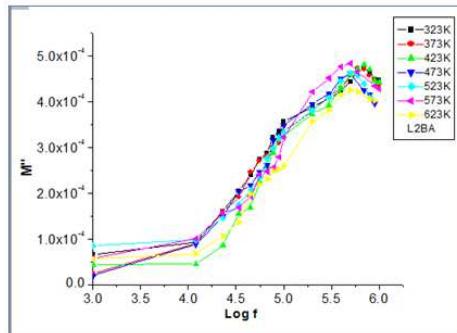
is significant at low frequencies which may be associated with the mobile ion polarization combined with electronic polarization. The low frequency dispersion of  $\epsilon'$  gradually increases with increase in temperature due to electrode polarization as well as thermal activation associated with  $\text{Li}^+$  ions in these glasses. The electrode polarization is significant at high temperature (473K – 623K) and masks bulk response of the glass in low frequency regime. When temperature rises, the dielectric dispersion shifts toward to higher frequency approach a constant value  $\epsilon''_\infty(\omega)$  which results from rapid polarization process occurring in the glasses under applied field [20]. Therefore mobile ions will not be able to rotate sufficiently rapidly, so their oscillation will lag behind the field, resulting decrease in dielectric permittivity ( $\epsilon'$ ). It is observed that dielectric constant increases with increase in temperature which is associated with decrease in bond energy [21]. All the plots merge at high frequency regime and independent behavior at high frequencies (10KHz – 1MHz) which is attributed to dielectric response of the glasses. The abrupt decrease in  $\epsilon'$  in the low frequency region may be due to interfacial effect such as space charge polarization. The lower frequency side dielectric constant ( $\epsilon'$ ) has power law dependence [22].

The variation imaginary dielectric constant ( $\epsilon''$ ) with frequency at various temperature is shown in figure 8. However it increases with increase in temperature, which is attributed to the increase in electrical conductivity of the glasses. The relaxation peaks at frequency 523Hz was encountered when measurement were done at 573K. The significant difference in the imaginary dielectric constant is observed at low frequency. However, all plots merge in the high frequency regime (above 10 KHz), such independent behavior at high frequency (10 KHz – 1 MHz) is attributed to intrinsic dielectric response of the glasses. The abrupt decrease in imaginary dielectric ( $\epsilon''$ ) in low frequency regime may be due to interfacial effect such as space charge polarization. The dielectric losses ( $\epsilon''$ ) at high frequencies are much lower than those occurring at low frequencies at specific temperature (above 473K). This kind of dependence of  $\epsilon''$  upon frequency is typically associated with losses by conduction. The nature of variation of dielectric parameters ( $\epsilon'$  &  $\epsilon''$ ) with frequency and temperature is found to be similar for all glass samples in the study. The values of dielectric parameters obtained from the graphs are depicted in the Table 2.

**Table 2: Dielectric Parameters of the L1BA-L5BA for Frequency 1 MHz**

Sample	Mole% $\text{Al}_2\text{O}_3$	$\epsilon'(\omega)$ 323K	$\epsilon_\infty(\omega)$ 323K	$\Delta\epsilon$ 323K	$\epsilon'(\omega)$ 623K	$\epsilon_\infty(\omega)$ 623K	$\Delta\epsilon$ 623K	$\epsilon''_\infty(\omega)$ 623K
L1BA	0	214.3	32.2	182.1	564	42.5	521	0.48
L2BA	5	130.7	20.2	110.5	161.8	25.0	136.8	0.25
L3BA	10	149.6	17.4	132.2	293.3	19.9	273.4	0.201
L4BA	15	84	29.5	54.5	243	34.5	218.5	0.364
L5BA	20	182	20.9	161.1	217.4	31.4	186	0.358

It is observed that pure sample (L1BA) have higher values of imaginary dielectric ( $\epsilon''$ ) hence electrical conductivity is high with respect to other samples. The magnitude of bulk polarization called dielectric strength is given by  $\Delta\epsilon = \epsilon_s(\omega) - \epsilon_\infty(\omega)$  as proposed by Sidebottom [23]. The value of  $\Delta\epsilon$  is high for the sample L1BA and value of imaginary constant also high shows that this glass composition has high conductivity. It is well agree with the result obtained from conductivity measurement. The variation of  $\epsilon'$  and  $\Delta\epsilon$  with content of  $\text{Al}_2\text{O}_3$  is depicted in figure 9.

Figure 7:  $\epsilon'$  v/s Log fFigure 8:  $\epsilon''$  v/s Log fFigure 9:  $\epsilon'$  and  $\Delta\epsilon$  v/s  $\epsilon''$  with  $\text{Al}_2\text{O}_3$ Figure 10:  $M'$  v/s log fFigure 11:  $M''$  v/s Log f

The real ( $M'$ ) and imaginary ( $M''$ ) part of dielectric modulus at different temperature are calculated using equations given above and depicted in the figure 10 & 11. It would be noticed from figure 10 that at low frequencies  $M'$  approaches zero at all temperatures under study, suggesting the suppression of electrode polarization and  $M'$  reaches maximum value corresponding to  $M'^\infty = (\epsilon_\infty)^{-1}$  due to relaxation process[24]. It is observed that the value  $M_\infty$  decreases with increase in temperature. The imaginary part of electric modulus ( $M''$ ) is indicative of energy loss under electric field. The imaginary part of dielectric modulus peak shifts to higher frequencies with increase in temperature, this suggest that involvement of temperature dependent relaxation process in the present glasses. The frequency region below  $M''$  peak indicate the range in which  $\text{Li}^+$  ions shifts to long distances. The two apparent relaxation regions appeared, the low frequency region being associated with hoping conduction and high frequency region is attributed to relaxation polarization process.

## CONCLUSIONS

The effect of compositional changes by addition of second former  $\text{Al}_2\text{O}_3$  into  $\text{Li}_2\text{O}:\text{B}_2\text{O}_3$  glass on electrical conductivity and dielectric properties has been investigated .It was observed that dc conductivity decreases with addition of  $\text{Al}_2\text{O}_3$  which is attributed to structural modification and formation of Al-O-B linkage, resulting in hinders the migration of  $\text{Li}^+$  ions. The maximum conductivity was observed for  $\text{Al}_2\text{O}_3$  free glass and it indicates that the mixed former effect does not exist in these compositions. The frequency and temperature dependence of dielectric properties of  $\text{Li}_2\text{O}:\text{B}_2\text{O}_3:\text{Al}_2\text{O}_3$  glasses have been investigated in the frequency range 10Hz – 1MHz. The dielectric relaxation peak was observed in the frequency dependent dielectric loss plots whose magnitude was composition dependent. The dielectric constant ( $\epsilon'$ ,  $\epsilon''$ ) increases with increase in temperature. The electrical properties were investigated and found obeying Jonscher's law and observed that the value of power exponent ( $s$ ) changes with composition which was reflected in variation of  $T_g$ .

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